

# Surface diffusion in reversed-phase liquid chromatography using silica gels bonded with $C_1$ and $C_{18}$ ligands of different densities

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## Abstract

Surface diffusion in reversed-phase liquid chromatography (RPLC) using silica gels bonded with  $C_1$  and  $C_{18}$  alkyl ligands of different densities was studied from the viewpoints of two extrathermodynamic relationships, i.e., enthalpy-entropy compensation (EEC) and linear free energy relationship (LFER). First, according to the four methods proposed by Krug et al., the values of surface diffusion coefficient ( $D_s$ ) were analyzed to confirm that an actual EEC resulting from substantial physico-chemical effects takes place for surface diffusion. Then, it was also demonstrated that a LFER is observed between surface diffusion and the retention equilibrium. The establishment of EEC and LFER suggests a mechanistic similarity of molecular migration by surface diffusion, irrespective of the alkyl chain length and the densities of  $C_1$  and  $C_{18}$  ligands. Finally, a thermodynamic model for the LFER based on the real EEC was used to estimate  $D_s$  values under various RPLC conditions. The  $D_s$  values can be estimated with a mean square deviation of about 25–30%. The agreement between the  $D_s$  values estimated and those experimentally measured suggests that the total mass flux by surface diffusion consists of the two contributions due to  $C_1$  and  $C_{18}$  ligands and that the contribution of each ligand is proportional to the ligand density.

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**Keywords:** Reversed-phase liquid chromatography; Alkyl ligand bonded silica gel; Surface diffusion; Extrathermodynamics; Enthalpy-entropy compensation; Linear free energy relationship

## 1. Introduction

Recently, different types of separation media and systems have been developed to attain fast chromatography with high efficiency. Under linear isotherm conditions, band broadening depends on the mass transfer kinetics of several rate processes involved in columns and packing materials, that is, axial dispersion, external (fluid-to-particle) mass transfer, intraparticle diffusion, and adsorption/desorption kinetics [1–5]. Additionally, intraparticle diffusion is usually explained by assuming the parallel diffusion by pore diffusion and surface diffusion [1,2,4]. The band broadening is predominantly influenced by the mass transfer kinetics in the packing materials under high flow rate conditions. However, compared with ample works on the retention equilibrium, there are not so abundant studies on the mass transfer kinetics in the columns, especially in the stationary phases.

It has been reported that surface diffusion has an important contribution to the molecular migration in the stationary phase [1,2,6,7]. Most molecules migrate in intraparticulate space by surface diffusion. The manner of surface diffusion depends on the retention behavior of the molecules because they migrate on the stationary phase surface under adsorbed state. In principle, chromatographic separations rest on the difference in the attractive interaction of the sample molecules with the stationary phase surface. Surface diffusion should be correlated with some essential characteristics of chromatographic separations. It is expected that detailed analyses of surface diffusion would provide an important information about the mechanism of chromatographic separations.

About 40 years ago, the significance of surface diffusion had already been suggested as one of important mass transfer processes [8]. In the field of chromatography, however, surface diffusion itself and its contributions to the mass transfer kinetics in the stationary phase and to the column efficiency are still not sufficiently recognized. Even now, there are few kinetic studies on chromatographic separations with considering the predom-

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**Nomenclature**

|                 |  |
|-----------------|--|
| $a$             | slope of the linear correlation between a thermodynamic property and $C_n$     |
| $A$             | slope of LFER  |
| $b$             | intercept of the linear correlation between a thermodynamic property and $C_n$ |
| $B$             | intercept of LFER  |
| $C$             | carbon content   |
| $C_n$           | carbon number in alkyl ligand  |
| $D_e$           | intraparticle diffusivity ( $\text{m}^2 \text{s}^{-1}$ )                       |
| $D_m$           | molecular diffusivity ( $\text{m}^2 \text{s}^{-1}$ )                           |
| $D_p$           | pore diffusivity ( $\text{m}^2 \text{s}^{-1}$ )                                |
| $D_s$           | surface diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )                   |
| $D_{s0}$        | frequency factor of surface diffusion ( $\text{m}^2 \text{s}^{-1}$ )           |
| $E_s$           | activation energy of surface diffusion ( $\text{J mol}^{-1}$ )                 |
| $\Delta G$      | free energy change ( $\text{J mol}^{-1}$ )                                     |
| $h$             | planck constant ( $\text{J s}$ )   |
| $\Delta H$      | enthalpy change ( $\text{J mol}^{-1}$ )  |
| $k_B$           | boltzmann constant ( $\text{J K}^{-1}$ )                                       |
| $k_f$           | external mass transfer coefficient ( $\text{m s}^{-1}$ )                       |
| $k_h$           | hindrance parameter  |
| $k_t$           | tortuosity factor  |
| $K$             | retention equilibrium constant ( $\text{m}^3 \text{g}^{-1}$ )                  |
| MS              | mean sum of squares  |
| MSD             | mean square deviation  |
| $N$             | number of data pairs ( $D_s^{\text{cal}}$ and $D_s^{\text{exp}}$ )             |
| $R$             | gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )                             |
| $\Delta S$      | entropy change ( $\text{J mol}^{-1} \text{K}^{-1}$ )                           |
| $T$             | absolute temperature ( $\text{K}$ )  |
| $T_c$           | compensation temperature ( $\text{K}$ )  |
| $T_{\text{hm}}$ | harmonic mean of experimental temperatures ( $\text{K}$ )                      |

*Greek letters*

|                 |   |
|-----------------|---|
| $\alpha_s$      | statistical level of significance                                 |
| $\delta_s$      | $D_s$ value normalized by $\sigma$ ( $\text{m}^2 \text{s}^{-1}$ ) |
| $\varepsilon_e$ | column void fraction (external porosity)                          |
| $\varepsilon_p$ | porosity of the stationary phase particle (internal porosity)     |
| $\lambda$       | distance between two equilibrium positions (m)                    |
| $\mu_1$         | first absolute moment (s)   |
| $\mu'_2$        | second central moment ( $\text{s}^2$ )                            |
| $\rho_p$        | particle density ( $\text{g cm}^{-3}$ )                           |
| $\sigma$        | alkyl ligand density ( $\mu\text{mol m}^{-2}$ )                   |

*Subscripts*

|                 |   |
|-----------------|---|
| 1               | condition 1                                   |
| 2               | condition 2                                   |
| con             | concurrency                                   |
| $C_1$           | contribution due to $C_1$ ligand              |
| $C_{18}$        | contribution due to $C_{18}$ ligand           |
| h               | enthalpy change                               |
| noncon          | nonconcurrency                                |
| ODS             | measured using the column #5                  |
| s               | entropy change                                |
| $T_{\text{hm}}$ | at harmonic mean of experimental temperatures |

|               |                              |
|---------------|------------------------------|
| TMS           | measured using the column #6 |
| $\varepsilon$ | measurement errors           |

*Superscripts*

|     |  |
|-----|--|
| cal | calculated   |
| exp | experimental   |
| REF | reference  |
| SMP | sample   |
| *   | thermodynamic parameters measured by analyzing temperature dependence of $D_s$ |

inant contribution of surface diffusion to the mass transfer in the stationary phase. We do not have yet enough information about the characteristics and mechanisms of surface diffusion in chromatography. Because of the quite important role of surface diffusion to intraparticle diffusion, the information is essential to develop superior packing materials for high performance and high speed separations.

This work deals with the characteristics and the mechanism of surface diffusion in reversed-phase liquid chromatography (RPLC) systems using silica gel particles bonded with  $C_1$  and  $C_{18}$  ligands of different densities. First, the mechanism of surface diffusion was discussed from the viewpoints of enthalpy-entropy compensation (EEC) and linear free energy relationship (LFER). Detailed analyses of surface diffusion data based on the four approaches proposed by Krug et al. [9–11] demonstrated that a real EEC is observed for surface diffusion and originates from substantial physico-chemical effects. The results of these extrathermodynamic studies indicate that the mechanism of surface diffusion is the same irrespective of the modification densities of  $C_1$  and  $C_{18}$  ligands. Then, it was attempted to use the results of the thermodynamic and extrathermodynamic studies on surface diffusion to predict  $D_s$  values under different RPLC conditions. The  $D_s$  values thus estimated agreed with those experimentally measured with a mean square deviation of 25–30%. This result suggests that the total flux by surface diffusion consists of the contributions of  $C_1$  and  $C_{18}$  ligands and that the contribution of each ligand is proportional to its density or coverage on the stationary phase surface.

**2. Experimental***2.1. Columns and reagents*

Table 1 lists some physical properties of five  $C_{18}$ -silica gel columns and packing materials. They are synthesized by the chemical modification of  $C_{18}$  ligands on the surface of the same base silica gel with end-capping treatment. Regarding the  $C_{18}$ -silica gel #5, no substantial increase in the carbon content was observed upon the end-capping with trimethylsilyl ligands. The bonding density of  $C_1$  and  $C_{18}$  ligands was intentionally changed. A column #6 was also used, which was packed with  $C_1$ -silica gel particles prepared using the same base silica gel. The six columns (6 mm id  $\times$  150 mm) were purchased from YMC

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